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Influence of Zinc Ions on Initial Stage of Localized Corrosion of Zn and Zn–Al Alloy Coated Steels with Photon Rupture Method

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The effect of pre-dissolved Zn ions in the solutions on the initial stage of localized corrosion after oxide films of Zn and Zn–Al alloy coated steels were removed by a photon rupture method, focused pulsed Nd-YAG laser beam irradiation, was investigated electrochemically. Zn ions can be inhibited dissolution of the Zn coated layer by precipitation of zinc hydroxide, which is formed by hydrolysis reaction of dissolved Zn ions in neutral buffer solutions. However, Zn ions do not affect the dissolution of a Zn–Al alloy coated layer. The absence of inhibition of the Zn–Al layer dissolution can be explained by pH change to lower values at the irradiated area by the hydrolysis reaction of the dissolved Al ions. The effect of Zn ions on corrosion inhibition of the coated layer by the photon rupture method established here was in good agreement with polarization experiments.

KEY WORDS: coated steel; localized corrosion; Zn ions; laser beam irradiation; corrosion resistance.

1. Introduction

Zinc related coated steels are historically widely used due to their excellent corrosion protection characteristics in many environments. The corrosion protection of the coated layers is ascribed to cathodic protection by a galvanic reaction between the coated layer and substrate,[1,2] and the formation of stable and compact corrosion products, which have high corrosion resistance. Composition of corrosion products formed on the steels caused by atmospheric corrosion has been investigated in various exposure conditions.[3]

The examination of abrupt destruction of passive oxide films and their repair is important for a better understanding of the localized corrosion of metals. Analysis of this behavior has been carried out by monitoring potential- and current-transients after mechanical stripping of oxide films.[4–8] The mechanical film stripping, however, poses problems of slow film stripping, contamination from the stripping tools, and stress and strain on the substrate. Recently, there are reports of film stripping by a photon rupture method (focused pulsed Nd-YAG-laser irradiation), which solves many of the problems involved in by mechanical film stripping. The irradiation with a pulsed laser beam is able to strip oxide film at extremely high rates without contamination from the removing tool of the film. This technique has been applied to localized corrosion of iron by Oltra *et al.*[9] and by Itagaki *et al.*,[10] and to localized corrosion of Zn and Zn–Al alloy-coated steel by Sakairi *et al.*[11–15] The authors have studied the behavior of artificial pits formed by photon rupture method on Zn and Zn alloy-coated steels, and reported that the direction of the rest potential shift was affected by the area ratio of the coated layer (Zn or Zn–Al alloy) to the steel in artificial pits.[16–18] Immediately after laser irradiation, the rest potential shifted to the negative direction while the coated layer was exposed to the solution, then, after the steel substrate becomes exposed to the solution, the rest potential shifted to the positive direction.

Recently, Kyo *et al.* reported that zinc ions in solution prevent the corrosion of the Zn coated layer and steel substrate.[19] However, it is not clear what the influence of zinc ions is on the very initial stage of localized corrosion, after the oxide film is broken mechanically or chemically. The purpose of this study is to investigate the effect of zinc ions on the initial stage of localized corrosion of Zn and Zn–Al alloy coated steels with photon rupture method.

2. Experimental

2.1. Specimen and Solution

Zinc (Zn), 5mass%Al–Zn (Zn–5Al) alloy and 55mass% Al–Zn (Zn–55Al) coated steel sheets (coated layer thickness of about 15 μm, Nippon Steel Co.) were cut into 15×20 mm coupons, and then were ultrasonic cleaned. For the laser experiments, the samples were dipped in a nitrocellulose/ethyl acetate solution two times to form an approximately 30 μm thick protective nitrocellulose film on the samples. The film works as an insulator to avoid electrochemical reactions at not laser irradiated area.

Solutions for the electrochemical measurements were 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ (pH=7.4) with 10 mol m^{-3} chloride ions, adjusted by adding NaCl and $ZnCl_2$. The solution volume of every electrochemical experiments was 0.2 dm^3 (200 cm^3).

2.2. Electrochemical Measurements

Polarization curves of without nitrocellulose film speci-

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mens in the presence and absence of zinc ions in the solution were also measured to determine optimum applied potentials for the laser experiments. The potential sweep rate was 0.33 mV s^{-1}.

After formation of the nitrocellulose film, the specimens were immersed in the solution and irradiated by a pulsed Nd-YAG laser (Sepctra Physics GCR-130) through a lens and a quartz window at constant potential. The laser beam was the second harmonic wave of wave length 532 nm, wave duration 8 ns, frequency 10 s^{-1}, and the laser power was adjusted to 30 mW in front of the lens. The current transient after irradiation was measured by a computer through an A/D converter. The irradiation time was also detected by a photo-detector. The sampling interval of current change was 0.02 ms and 2 ms for short and long polarization experiments respectively. The measured current was converted to current density using the area of the pit, as a circle, after each experiment.

The electrochemical measurements were carried our several times and scatterings of the data at each experiment were very small. A saturated Ag/AgCl electrode was used as a reference electrode to measure the electrochemical data.

2.3. Surface Observation

The specimen surfaces were examined by a con-focal scanning laser microscope (CSLM; 1SA21, LASERTEC Co.) before and after the experiments. The pit depth was measured with the analysis function of the CSLM.

3. Results

3.1. Polarization Behavior

Figure 1 shows polarization curves of Zn coated steels (without nitrocellulose film) in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl and with 5 mol m^{-3} $ZnCl_2$. The chloride ion concentrations of both solutions are the same. The rest potential in the $ZnCl_2$ solution is slightly higher than that in the NaCl solution. When polarization is started, the current increases with potential in both solutions, and after the polarization experiments, there are a lot of pits, which were covered with corrosion products in both solutions. There is no clear current difference between the solutions at low potentials. However, at higher potentials (<-0.65 V), it is a clear that the current of Zn ions containing solutions is lower than that of Zn ions free solutions. This result suggests that Zn ions inhibit dissolution of the Zn coating itself especially at the high potential range, suggesting that a specific concentration of Zn ions is needed to activate the corrosion inhibition function of Zn ions.

Figure 2 shows polarization curves of Zn–5Al and Zn–55Al alloy coated steels (without nitrocellulose film) in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl and with 5 mol m^{-3} $ZnCl_2$. When polarization is started, the current increases with potential in all experiments, and there are a lot of pits, which were covered with corrosion products after all experiments. Neither the rest potential nor the current is change by adding Zn ions. This result suggests that Zn ions do not affect corrosion of Al containing coatings, in another way small amounts of aluminum ions hinder the corrosion inhibition function of Zn ions.

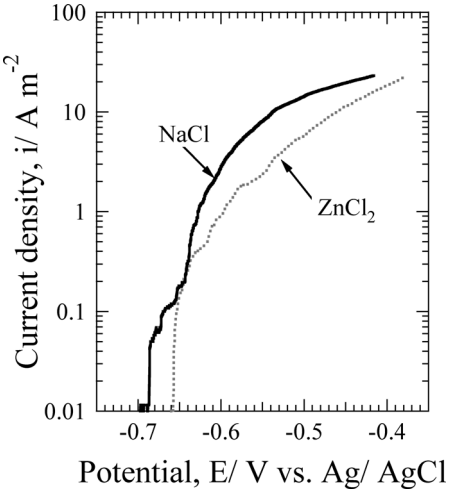

Fig. 1. Polarization curves of Zn coated steels in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

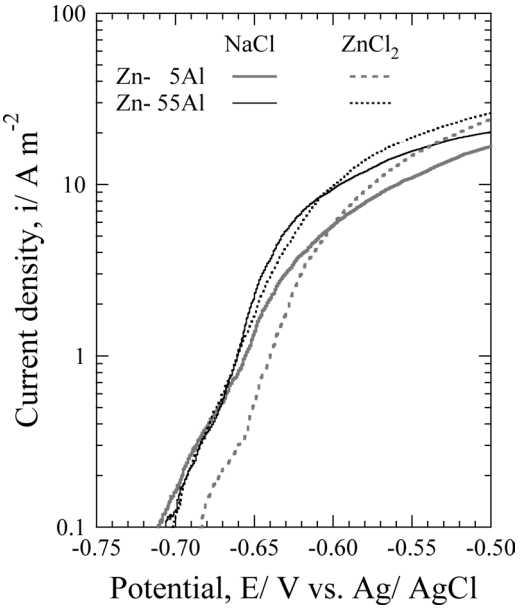

Fig. 2. Polarization curves of Zn–5A- and Zn–55Al coated steels in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

From the polarization experiments, the pitting corrosion occurs just after anodic potential was applied in both coatings. Therefore the applied potential to investigate the effect of Zn ions and potential on localized corrosion was determined as -400 mV and -600 mV, and these potentials are equal to or higher than pitting potential. This means that when the films were removed by laser beam irradiation, metals of coatings should be dissolved to form corrosion pit and corrosion products.

3.2. Current Transients of Zn Coated Steel

Figure 3 shows changes in current density after laser irradiation up to 1 s at -600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$. The current increases instantaneously through a maximum, at about 0.4 ms, decreases, and then

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the current starts to increases again after about 20 ms in both solutions after the laser irradiation. This shows that there is oxide film repair at the initial stage after laser irradiation, but after some time, localized corrosion starts in both solutions, because this potential is almost the same as pitting potential. This time delay may be same as the incubation time for traditional potentiostatic pitting corrosion experiments. The current transients of both solutions are similar, in good agreement with the current differences in the polarization results (Fig. 1) at low potential. This figure also shows that 1 s measuring time is not long enough for to investigate the effect of Zn ions on inhibition of corrosion.

Figure 4 shows changes in current density after laser irradiation up to 800 s at −600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$. In NaCl solution, when the film is removed, the current increases instantaneously through a maximum then decreases, and remains unchanged from 0.1 s to 10 s; after 10 s, the current starts to increase again, shows maximum and then decreases. After the experiments corrosion products were formed at the irradiated area, therefore the current change may due to formation of the corrosion products inside the pits. The current change in $ZnCl_2$ solution is the same as in NaCl solution. This figure does not clear to show the effect of Zn ions on the corrosion of the Zn layer at this potential.

The corrosion products and nitrocellulose film were removed before the CSLM observation. **Figure 5** shows CSLM contrast images after the experiments in NaCl solutions, (a) up to 1 s, and (b) up to 800 s. The shape of pit does not change with time, however, the size increases with polarization time. There were no differences in the size and shape of the pits at the same time points in the two solutions. The Zn coating around the irradiated area, where still nitrocellulose film was covered, also dissolved. However, other Zn coating surface did not dissolve during the experiments. These results mean that the measured currents are related to local dissolution of laser irradiated Zn coating.

Figure 6 shows changes in current of Zn coated steel after laser irradiation up to 1 s at −400 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$. At the initial, the current decreases slightly, and then the current increases again after 2 ms in both solutions. The current in NaCl solution is lager than that in $ZnCl_2$ solution. This behavior is in good agreement with current differences in the polarization results (Fig. 1)

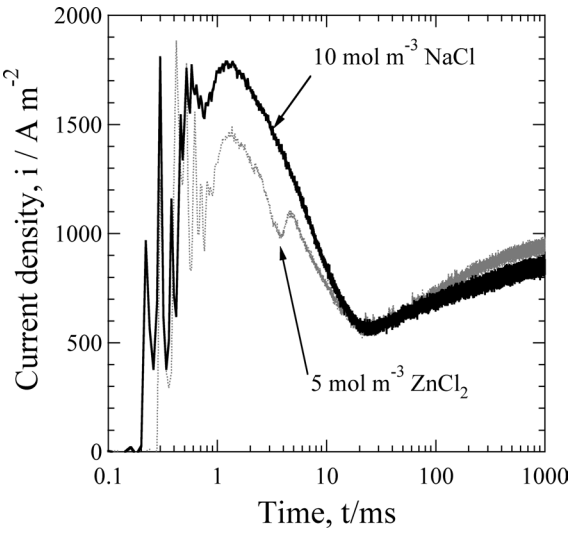

Fig. 3. Changes in current of Zn coated steels after laser irradiation up to 1 s at −600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

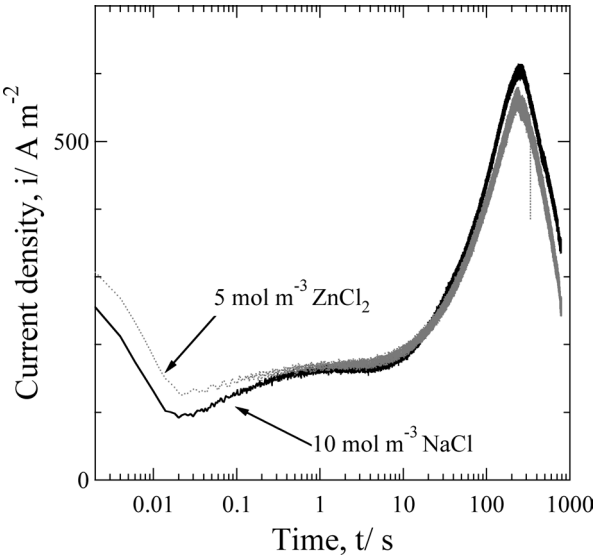

Fig. 4. Changes in currents of Zn coated steels after laser irradiation up to 800 s at −600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

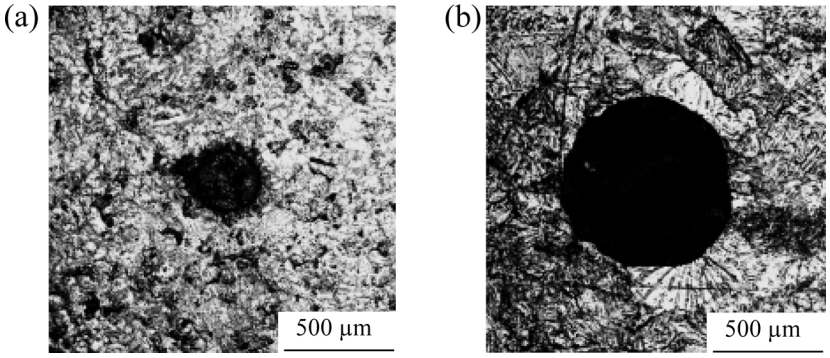

Fig. 5. CSLM contrast images of after the laser experiments in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl, after laser irradiation, (a) up to 1 s, and (b) up to 800 s. The corrosion products and nitrocellulose film were removed before the CSLM observation.

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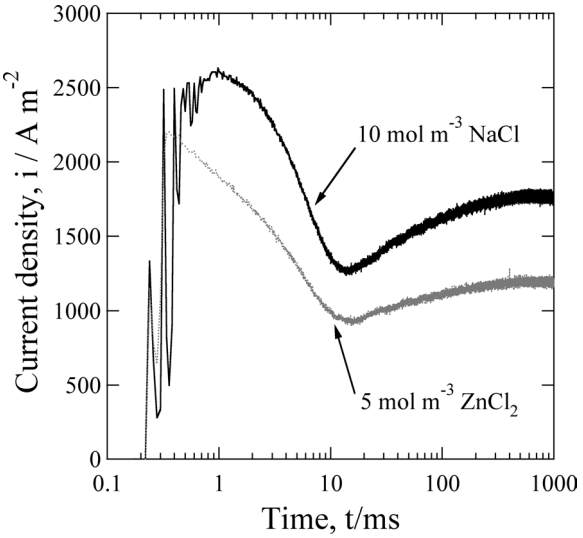

Fig. 6. Changes in current of Zn coated steels after laser irradiation up to 1 s at −400 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

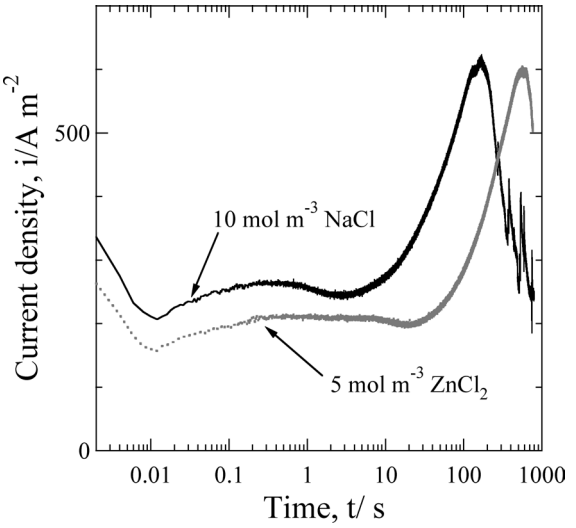

Fig. 7. Changes in current of Zn coated steels after laser irradiation up to 800 s at −400 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

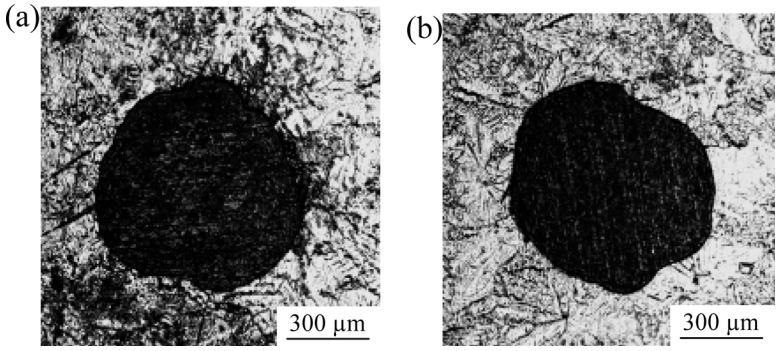

Fig. 8. CSLM contrast images after the experiments of Fig. 7, (a) in NaCl and (b) in $ZnCl_2$. The corrosion products and nitrocellulose film were removed before the CSLM observation.

at high potentials.

Figure 7 shows changes in the current of Zn coated steels after laser irradiation up to 800 s at −400 mV. The applied solutions are the same as in Fig. 6. When the film is removed in the NaCl solution, the current increases instantaneously through a maximum then decreases with time, the current shows an almost constant value up to 10 s. After more than 10 s, the current starts to increase and then decreases again. The irradiated area was covered by corrosion product after the experiments. These change is the same as the current changes in $ZnCl_2$ solutions, but the current measured in the $ZnCl_2$ solution is smaller than the current measured in the NaCl solution. There is clearly an effect of Zn ions on the corrosion of the Zn coated layer at this potential. **Figure 8** shows CSLM contrast images after the experiments, (a) in NaCl and (b) in $ZnCl_2$ in Fig. 7. The corrosion product and nitrocellulose film were removed before the observations. The pit sizes and shapes are almost the same in both solutions, however the depth became deeper with polarization time. Therefore, the resumption of the increase in the current is related to growth of the pits and the decrease is related to formation of corrosion products inside the pits where they inhibit the dissolution of Zn. The measured pit depth was about 20 μm, which is more than the coating layer, substantiating that the morphology inside the pit is different form that of in Fig. 5.

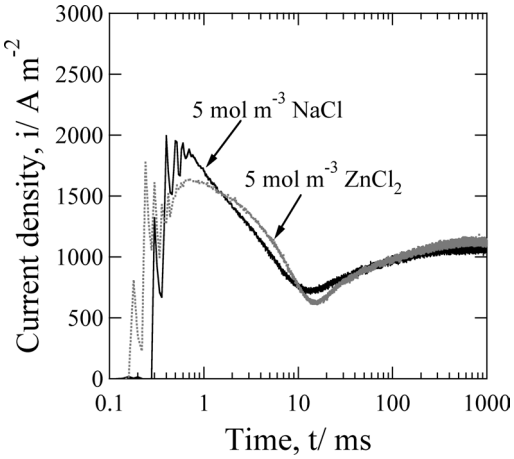

Fig. 9. Changes in current density of Zn–5Al alloy coated steels after laser irradiation up to 1 s at −600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

3.3. Current Transients of Zn–Al Alloy Coated Steels

Figure 9 shows the changes in current density of the Zn–5Al alloy coated steels after laser irradiation up to 1 s at

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−600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$. The current increases instantaneously, through a maximum at about 0.4 ms, then decreases slightly, and increases again after 20 ms in both solutions after the laser irradiation. The current transient in the NaCl solution varies less than that in $ZnCl_2$ solution, suggesting that Zn ions do not affect on the dissolution rate of the aluminum containing coated layer. Almost same current transients were observed with Zn–55Al alloy coated steels.

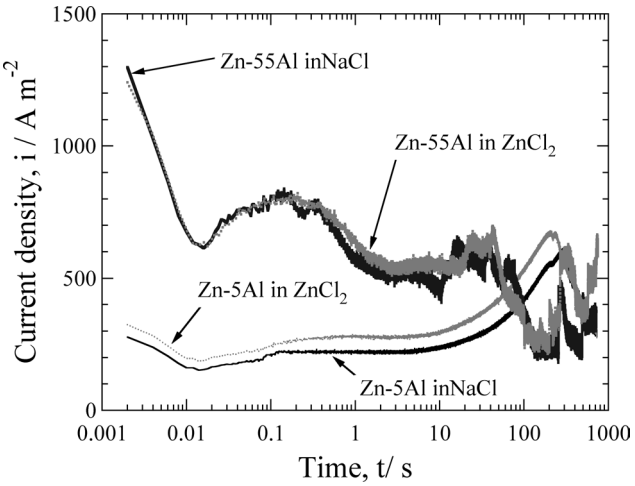

Fig. 10. Changes in current density of Zn–5Al or Zn–55Al alloy coated steels after laser irradiation up to 800 s at −600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$.

Figure 10 shows the changes in the current density of the Zn–5Al and Zn–55Al alloy coated steels after laser irradiation up to 800 s at −600 mV in 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ with 10 mol m^{-3} NaCl or with 5 mol m^{-3} $ZnCl_2$. In all experiments, the current increases initially and then decreases, then after a while the current shows increases and decreases. The white corrosion products and gas bubbles were formed at the irradiated area during all experiments. Compared with Fig. 9, the depth at irradiated area became deeper. Therefore, the second current increase corresponds to the start of localized corrosion and the second current decrease is related to the formation of corrosion products at the irradiated area. The current of the Zn–55Al coated steels, especially after 10 s, has large and long cyclic fluctuations in both solutions. In previous work, we reported that these fluctuations were related to gas evolution, growth and detachment.[13–15] From this figure, the corrosion protection effect of Zn ions is hindered if the layer has small amount of Al, but the mechanism is not fully elucidated.

4. Discussion

4.1. Influence of Zn Ions

Figure 11 shows a schematic representation of the possible mechanism of the effect of Zn ions on dissolution of the coated layer. Because of a buffer reaction and pH, the concentration of Zn ions in the solution before the experiments is same as the saturation limit of 0.5 kmol m^{-3} H_3BO_3–0.05 kmol m^{-3} $Na_2B_4O_7$ buffer solution.[20] It is difficult to measure and precisely estimate the pH change at the coating surface after the irradiation. However, it is possible to

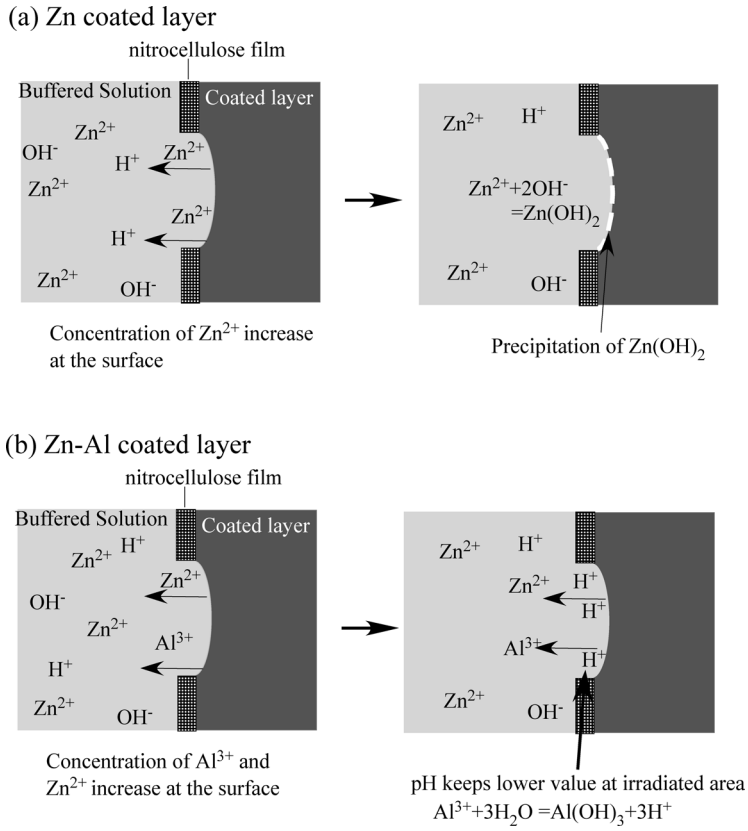

Fig. 11. Schematic representation of the effect of Zn ions on corrosion of the coated layer, (a) Zn coated layer and (b) Zn–Al alloy coated layer.

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make rough calculation of the surface pH change.

In the case of Zn coated layers (a), Zn was dissolved at very high rates and the concentration of Zn ions increased just after the laser irradiation. As dissolution of Zn, the pH would change to lower value by the hydrolysis reaction of Zn ions (reaction (1)).

$$Zn^{2+}+2H_2O=Zn(OH)_2+2H^+ \quad \text{.....(1)}$$

The charge up to 1 s after the laser irradiation is about 1 000 C/m^2 and a diffusion length of metal ion may be shorter than 10 μm, therefore, the estimated Zn ion concentration is about 0.04 kmol m^{-3}. Using this concentration, the estimated pH is about 5.3 at the irradiated surface in the initial stage.[20] However, the solution here buffers the reaction of pH change and the initial pH is sufficiently high, therefore the solution would be maintain pH around 7. Because of dissolution of Zn ions, reaction (2) would be dominant in neutral buffer solutions and $Zn(OH)_2$ would precipitate on the irradiated surface.

$$Zn^{2+}+2OH^-\Rightarrow Zn(OH)_2\downarrow \quad \text{.....(2)}$$

The precipitation reaction rate would depend on the pH at the metal solution interface. This precipitated film may inhibit the dissolution of the Zn layer.

The electrochemical results show that Al cannot form protective films such as $Al(OH)_3$ or Al_2O_3 in the experimental conditions. With an Al containing coating (b); Al also dissolves to increase the concentration of Al^{3+} ions near the irradiated surface area. Then, the hydrolysis reaction of Al^{3+} ions takes place

$$Al^{3+}+3H_2O=Al(OH)_3+3H^+ \quad \text{.....(3)}$$

If the Al ion concentration is about 0.01 kmol m^{-3} at the surface in the initial stage, the estimated pH is about 3.7. This means that the ability of Al ions to change pH is lager than that of Zn ions. It is difficult to precisely estimate the pH change at the coating surface after the irradiation, however, when Al ions dissolve form the coating, it would change pH to become low enough to hinder the precipitation reaction (2). This means that $Zn(OH)_2$ no longer forms a precipitation film on the coating surface, therefore Zn ions would not inhibit the corrosion of Zn–Al alloy coating layer.

4.2. Influence of the Laser Irradiation on Electrochemical Reactions

The pulse duration of the used Laser was 8 ns, sampling rate of the current transient was 0.2 ms and the main anodic reaction is dissolution of metals, therefore, it is difficult to measure the photo-excitation phenomena of the electrochemical reactions.

P. Krehl *et al.*, calculated that it needs about 10 ms to reach final temperature after the irradiation in vacuum.[21] The calculation does not take into account phase change and effect of environment, such as water. If we consider these effects for the calculation, the temperature change rate should be faster than the rate of P. Krehl *et al.* were reported. In previous paper,[12,13] we have reported that oxide film formation kinetics was followed by inverse logarithmic low after the current peak (about 1 ms after laser irradiation) in chloride free solutions at constant potentials. This means that there is any heat affect on re-passivation kinetics. Therefore, the surface temperature, which was produced by the laser irradiation, may not affect electrochemical reaction.

5. Conclusions

(1) At high potentials, Zn ions decrease the corrosion rate of the initial stage of localized corrosion of Zn coated steels in neutral borate buffer solutions with Cl^- ions, and this can be explained by precipitation of Zn-hydroxide.

(2) Zinc ions do not affect the initial stage of localized corrosion of Zn–5Al and Zn–55Al coated steel at constant potentials in neutral borate buffer solutions with Cl^-. This can be explained by pH shifting to lower values around the irradiated area by a hydrolysis reaction of the dissolved Al ions.

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